Interconversion between guanine quartet and triad on the Au(111) surface

Electronic supplementary information

Yuanqi Ding,[a] Lei Xie,[a] Donglin Li,[a] Hanlin Shen,[a] Cuiyu Li [b] and Wei Xu*[a]

[a] Interdisciplinary Materials Research Center , College of Materials Science and Engineering, Tongji University, Shanghai 201804, P. R. China

[b] Advanced Computing East China Sub-Center, Suma Technology Co., Ltd., Kunshan 215300, P. R. China

* Correspondence: xuwei@tongji.edu.cn

STM images

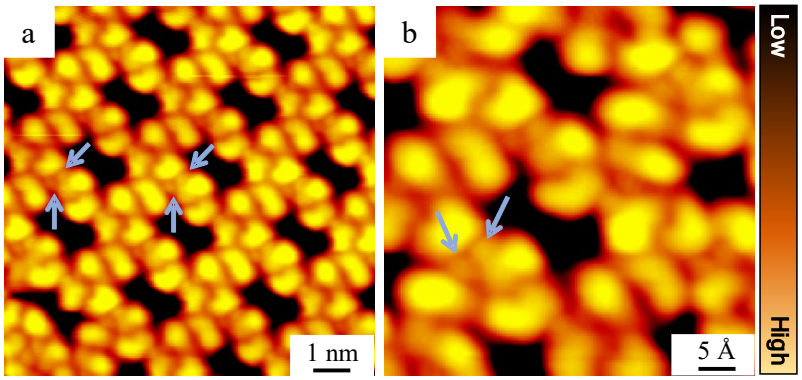


Figure S1. STM images of the $9eG_3Na_2$ network with a special tip state, in which the Na cations can be visible as indicated by blue arrows. Scanning conditions: I_t = 0.9 nA, V_t = -1400 mV.

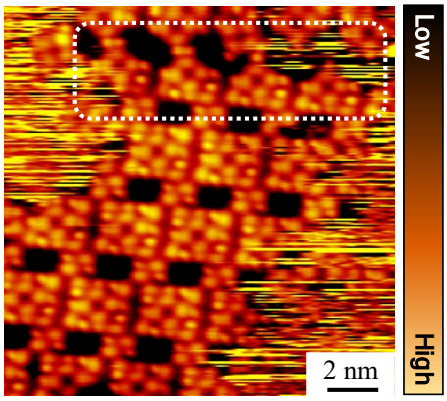
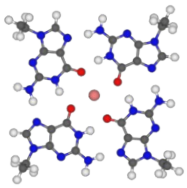
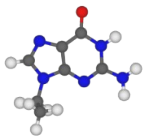


Figure S2. STM image of hybrid supramolecular network composed of $9eG_3Na_2$ and $9eG_4Na_1$ on Au(111). The outlined defects help to ensure the composition of two kinds of elementary motifs, in which some $9eG_3Na_2$ motifs are missing. Scanning conditions: I_t = 0.8 nA, V_t = 1480 mV.

DFT calculations

Table S1. Details of the DFT calculations.			
			
$9eG_4Na_1$ -586.9833 eV	**$9eG_3Na_2$** -439.8597 eV	**9eG** -145.2900 eV	**Na** -0.0074 eV

E_b of $9eG_4Na_1$ motif

E_b = (-586.9833 - (-145.2900×4) – (-0.0074))/4 = -1.4540 eV/molecule

E_b of $9eG_3Na_2$ motif

E_b = (-439.8597 - (-145.2900×3) – (-0.0074×2))/3 = -1.3283 eV/molecule

The above detail data shows that the E_b value of the $9eG_4Na_1$ motif is calculated to be 1.45 eV per molecule, and the E_b value of the $9eG_3Na_2$ motif is calculated to be 1.33 eV per molecule, which is in accordance with the experimental results.

Methods

All STM experiments were performed in a UHV chamber (base pressure 1×10^{-10} mbar) equipped with a variable-temperature, fast-scanning "Aarhus-type" STM using electrochemically etched W tips purchased from SPECS,[1,2] a molecular evaporator and an e-beam evaporator, and other standard instrumentation for sample preparation. The Au(111) substrate was prepared by several cycles of 1.5 keV Ar^+ sputtering followed by annealing to 800 K for 15 min, resulting in clean and flat terraces separated by monatomic steps. The 9eG molecule (purchased from Sigma-Aldrich, purity > 98%)

was loaded into the glass crucible in the molecular evaporator. After a thorough degassing, the molecules are deposited onto the Au(111) surface by thermal sublimation. The alkali metal sodium was evaporated from Alvasource (from Alvatec) *via* conventional resistance heating after fully degassing. The sample was thereafter transferred within the UHV chamber to the STM, where measurements were carried out at ~100-150 K. All of the STM images were further smoothed to eliminate noises.

The calculations were performed in the framework of DFT by using the Vienna *ab initio* simulation package (VASP).[3, 4] The projector-augmented wave method was used to describe the interaction between ions and electrons;[5, 6] the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) exchange-correlation functional was employed,[7] and van der Waals interactions were included using the dispersion-corrected DFT-D3 method of Grimme.[8] The atomic structures were relaxed using the conjugate gradient algorithm scheme as implemented in the VASP code until the forces on all unconstrained atoms were ≤ 0.03 eV/Å.

Reference

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